



Using different materials as a permeable reactive barrier for remediation of groundwater contaminated with landfill's leachate

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ABSTRACT

The present study investigates the utilization of the waterworks sludge by-product that generated from water supply treatment plant for the remediation of simulated groundwater contaminated with leachate spilled from the sanitary landfill by permeable reactive barrier (PRB) technology. Batch sorption experiments were conducted for describing the interaction between the acetogenic phase (pH = 5.5 ± 0.1) of leachate contaminated with cadmium (Cd(II)), ammonia nitrogen (NH₃-N) or dissolved organic matter (COD) and waterworks sludge. Also, conventional sorbents such as the activated carbon and amberlite ion-exchange resin were tested to evaluate their ability in comparison with waterworks sludge in the remediation process. Results proved that the Langmuir model describes well the sorption data with maximum sorption capacities of 5.634, 14.908 and 3.938 mg/g for Cd(II) onto sludge, NH₃-N onto resin and COD onto activated carbon, respectively. The batch and column tests signified that the sludge, resin, and carbon can be used for removing Cd(II), NH₃-N, and COD, respectively. The multi-layered bed of sorbents under consideration has a remarkable ability in the remediation of a leachate contaminated with Cd(II), NH₃-N, and COD. Finally, the Yan model is more representative than Thomas and Belter models for characterization of the contaminants propagation in the column packed with single sorbent.

Keywords: Landfill leachate; Permeable reactive barrier; Waterworks sludge; Isotherm; Contamination

1. Introduction

Sanitary landfill is the most techniques used for the management and elimination of municipal solid waste around the world because it is a low-cost effective method and simple in operation. The disposal of wastes in the areas that not have the specifications for the dumping process may lead to the migration of spilled leachate to a large extent within the subsurface environment. This will affect significantly the groundwater quality and loss of composted soil

is a popular example of this effect [1]. Solid wastes such as scrap metals, metallic devices, batteries and electronic wastes found in landfills are the main sources of heavy metals in landfill leachate. Non-essential metals such as lead, cadmium, chromium, and mercury are highly toxic, even at very low concentrations. Moreover, these metals have been shown to accumulate in plant and animal tissues, therefore even low exposure concentrations can bio-accumulate during prolonged exposures to cause toxicity [2]. Previous studies such as Kjeldsen et al. [3] signified that the average

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concentrations of dissolved organic matter (COD), $\text{NH}_3\text{-N}$, and Cd(II) in the real leachate are equal to 22,000, 740 and 6 mg/L, respectively for acetogenic phase. Groundwater is one of the most widespread sources of water and its contamination due to spillage of hazardous wastes from landfills and other ponds have become a major environmental concern. Permeable reactive barrier (PRB) system is in-situ treatment technology that can be implemented for remediation of groundwater on-site without pumping the water to the surface of the ground [4].

The degradation of leachate can be occurred in four successive steps: (1) aerobic step, (2) hydrolysis and fermentation step, (3) anaerobic acetogenic step, and (4) anaerobic methanogenic step [3]. The acidic phase of the leachate is chemically aggressive and enhanced the solubility of many compounds [5], therefore, this study focused on landfill's leachate generated during the acetogenic phase. Leachate has relatively high concentrations of COD, ammonia nitrogen and heavy metals where the choice of the suitable sorbent is related to its ability in the removal of these contaminants present together simultaneously. Zeolite PRB was used to remove the cadmium from simulated contaminated groundwater. One dimensional finite difference model was developed to describe the migration of this contaminant in the barrier and sand aquifer [6]. Determination of the best conditions for the preparation and treatment of landfill leachate from banana pseudo-stem based activated carbon was achieved. The combined effect of three parameters namely; activation time, temperature and impregnation ratio was optimized using response surface methodology based on Box–Behnken [7]. The potential application of fungal biomass as a low-cost sorbent for the removal of toxicity from raw leachate was determined [8]. Natural materials such as aquifer sand, peat, and the commercial material (Burgess Iron Removal Media (BIRM)) were evaluated for the treatment of leachate resulted from the Taman Beringin Landfill/Malaysia using the column tests. The results signified that the BIRM sorbent has a higher adsorption capacity for Fe, Cr, Ni, and Cu compared with aquifer sand and peat [9]. The removal efficiencies of ammonia nitrogen from simulated wastewater by waste foundry sand based on 120 batch experiments were modeled by a three-layer artificial neural network technique. The sensitivity analysis signified that the most influential parameter is the contact time with relative importance equal to 36.9% [10]. Granular activated carbon (GAC) is the most effective sorbent that has high capacities for removing a wide range of organic and inorganic contaminants due to its surfaces, which typically have high densities of phenolic and carboxylic groups [11]. Also, the ion-exchange resin can be used as an excellent sorbent to remove $\text{NH}_3\text{-N}$ from the contaminated water as described in the previous studies [12,13]. Although these materials are the most suitable adsorbent for contaminants removal, their widespread use was limited due to the high cost [14,15]. So, sludge has been used in water and wastewater treatments as a low-cost sorbent replacing GAC and resin.

Several million tons of waterworks sludge can be produced every year in Europe alone and this number may be expected to increase dramatically in the future. This sludge is classified by the European legislation as “nonhazardous” and, accordingly, it can be disposed of together with municipal

solid wastes. The cost of sludge disposal has increased in some countries, while in other countries it is returned to the river and this can be increased the turbidity of the water. Accordingly, water companies have been seeking cheaper options to minimize the problems associated with sludge removal [16]. So, the use of waterworks sludge as a reactive material in the PRB is one of these options. The sludge is primarily composed of Fe/Al hydroxides which are often amorphous species; and it contains organic and suspended matters, inorganic matter, chemical, and humic substances, various microbial consortia, and coagulant products where these components play a significant role in the sludge's reactivity [17,18]. Effective management of waterworks sludge in an economically and environmentally sustainable manner remains a significant social and environmental concern due to the increase in the potable water as a result of rapid growth for world population and urban expansion. Various intensive practices such as adsorbent for phosphorous, fluoride, perchlorate, textile dye, and others have been employed to reuse this sludge for filling the gap between successful drinking water treatment process and environmentally friendly alum sludge management [19].

Many studies have investigated the possibility of using the dewatered waterworks sludge for heavy metals removal from landfill's leachate [20]. These studies certified that this sludge has large surface areas and high affinity for heavy metals such as cadmium, chromium, copper, zinc, lead [21,22]. Unfortunately, previous studies have not investigated the possibility of using the waterworks sludge in the PRB technique for treating the groundwater contaminated with leachate. Accordingly, the focal point of this study is examined the using of the sludge generated as byproduct from water supply treatment plant in the PRB for remediation of groundwater contaminated with landfill's leachate under different operation conditions for batch and continuous modes of operation in comparison with commercial activated carbon (CAC) and ion-exchange resin conventional materials.

2. Experimental work

2.1. Sorbents

Waterworks sludge was collected from the Al-Weihdaa water treatment plant (WTP)/Baghdad/Iraq. This plant is used alum salts in the purification of the raw water. The sludge was air-dried for three days and, based on sieve analysis, the size range (1–0.063 mm) was chosen with a geometric mean diameter of 0.25 mm [23]. The hydraulic conductivity, bulk density, and porosity of this material have the values of $2.929 \times 10\text{m/s}$, 1.06 g/cm and 0.42 , respectively. The sludge was also characterized using X-ray diffraction (XRD) analysis test to determine its mineralogy.

CAC was purchased from the local market and sieved to obtain the particle size distribution approximately identical to that of sludge. The hydraulic conductivity, bulk density, and porosity of CAC are equal to $6.794 \times 10\text{ m/s}$, 0.66 g/cm and 0.5 , respectively with Brunauer–Emmett–Teller surface area greater than 850 m/g .

Also, a synthetic ion-exchange resin (Amberlite IR120 Na) which classified as strong acid cation exchanger (obtained

from DOW Chemical Co., USA) was chosen. It was washed with distilled water to remove any undesired impurities and, then, dried at 105°C for 12 h. It was pretreated with a strong acid (0.1 N HCl) to convert the cation exchanger to H form [13]. Thereafter, distilled water was used for washing the resin to remove the acid and the resin can be dried at room temperature. The resin's hydraulic conductivity, bulk density, and porosity are equal to 4.24×10 m/s, 0.84 g/cm³ and 0.55, respectively. The porosity of all sorbents used in the present tests is determined for packed columns, while the particle size distribution for the ion-exchange resin is identical for that distribution of sludge and CAC mentioned previously.

2.2. Contaminants

Three types of stock solutions were prepared to achieve the requirements of this study as follows:

- Two stock solutions of cadmium and ammonia with a concentration of 1,000 mg/L were prepared separately by dissolving 2.744 g of Cd(NO₃)₂·4H₂O and 3.819 g of NH₄Cl in 1 L of distilled water, respectively.
- COD with a concentration of 9,000 mg/L was prepared by dissolving 11.535 g of sodium acetate anhydrous in the 1 L of distilled water.

All stocks solutions were diluted to get the desired concentration and adjusted to acidic conditions (pH of 5.5) to represent the acetogenic phase of leachate using 0.1 M HCl or NaOH as required. Finally, the synthetic leachate is prepared using the same procedure adopted in [24] for the acetogenic phase and the constituents of this leachate are mentioned in Table 1. The concentrations of COD, NH₃-N, and Cd(II) in the prepared leachate have the values in the ranges 6,520–8,700 mg/L, 510–544 mg/L, and 32 ± 2 mg/L, respectively. Indeed, the synthetic leachate considers a suitable choice for present experimental work because it is difficult to obtain the actual leachate in the acetogenic phase; also, degradation of the actual leachate can be caused a continuous change in the initial concentrations of the leachate contaminants.

2.3. Batch experiments

Several 250 mL conical-flasks were used and each one was filled with 100 mL of Cd(II) solution where the initial concentration of metal equal to 50 mg/L. Different quantities of sludge 0.5, 1, 5, 10, and 20 g were added to the solutions in the flasks. The solution in each flask was kept stirred on an agitation speed at 200 rpm for 2 h using orbital shaker (Edmund Bühler SM25, German). The treated solution was filtered using filter paper type (JIAO JIE 102, China) and 10 mL of this solution was analyzed to measure the concentration of Cd(II) using atomic absorption spectrophotometer (AAS, Sens AA, Australia). The experiments for specifying the best contact time were carried out by withdrawn samples periodically through the periods ranged from 10 to 120 min. Additional tests were conducted to study the effect of initial concentration and agitation speed on the removal efficiency of cadmium where concentrations are changed from 50 to 250 mg/L, while agitation speeds have values of 0, 50, 100, 150, 200, and 250 rpm.

Table 1

Composition constituents of synthetic landfill leachate per liter

Constituents	Values
Acetic acid (99%) (mL)	7
K ₂ HPO ₄ (mg)	30
KHCO ₃ (mg)	312
K ₂ CO ₃ (mg)	324
NaNO ₃ (mg)	50
NaHCO ₃ (mg)	3,012
CaCl ₂ ·2H ₂ O (mg)	2,882
MgCl ₂ ·6H ₂ O (mg)	3,114
MgSO ₄ (mg)	156
NH ₄ HCO ₃ (mg)	2,439
CO(NH ₂) ₂ (mg)	695
3CdSO ₄ ·8H ₂ O (mg)	80

The experiments described previously were repeated to investigate the ability of sludge to remove NH₃-N (600 mg/L) and COD (8,660 mg/L) from aqueous solution using high values of sludge dosages (≥ 50 g/100 mL). The remaining concentrations of NH₃-N in the solution were measured using KJELTEC AUC 1030 analyzer by distillation and titration method. The COD concentrations were measured by the photometer (Lovibond MultiDirect Sn 11/3942, Germany) and this procedure applied widely in the previous studies such as [25–27]. Results proved that the sludge is suitable for remediation of aqueous solutions contaminated with cadmium and low removal efficiency was achieved for NH₃-N while it was not suitable to remove COD. This means that other reactive materials must be adopted to achieve the acceptable removal for NH₃-N, and COD. So, CAC and amberlite ion-exchange resin were adopted and tested in the set of experiments similar to those mentioned previously where dosages of sorbent were ranged from 0.5 to 70 g per 100 mL for different values of initial concentrations. The removal efficiency (*R*) for all contaminants was determined by:

$$R = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (1)$$

where *C*₀ and *C*_{*e*} are the initial and final concentrations of contaminant (mg/L).

The quantity of contaminant sorbed by the solid phase, *q_e* (mg/g) can be evaluated by:

$$q_e = (C_0 - C_e) \frac{V}{m} \quad (2)$$

where *m* is the quantity of reactive material added to the flask (g) and *V* is the volume of contaminated water (L).

2.4. Continuous experiments

Fixed bed column studies were conducted using an acrylic glass column of 5 cm inner diameter and 70 cm length

schematically shown in Fig. 1. The column was filled with a 30 cm depth of reactive media and it is supported with two screens at the bottom and top of the bed. Two ports for taking the samples were equipped with the column and these ports are located at distances of 10 (P1) and 30 cm (P2) measured from the bottom. The ports were used to withdrawn the aqueous solution samples periodically for a duration not exceeding 24 h. The collected samples, with a volume of 2.5 mL, were filtered immediately and kept at 4°C until achieving the analysis for COD, NH₃-N, and Cd(II).

The column was packed with single bed of sludge, CAC or resin, however, two additional column tests were conducted to simulate the migration of leachate through multi-layered configuration bed consisted of sludge, resin and CAC arranged in the series scheme with dimensions of (2, 8 and 20 cm for bed 1) and (5, 5 and 20 cm for bed 2), respectively. The bed was saturated with distilled water at the beginning of the test and, then, the contaminated aqueous solution was continuously introduced from the bottom of the bed using a storage tank and peristaltic pump (Longer pump BT300-2J) with a flow rate of 3 mL/min at room temperature. This value of flowrate was selected to satisfy the laminar flow, that is, Reynolds number (R) < 1–10 [28], which is the predominant situation for groundwater flow in the porous medium. The flow was upward to ensure fully saturated, to prevent channeling and to avoid entrapped air. The experiments can be considered a good representation for one-dimensional migration of contaminants in the real operation of PRB where the concentration of contaminants in the affluent and breakthrough time is the most adequate parameters for evaluating the performance of the barrier [29].

3. Modeling of batch and continuous outputs

3.1. Models of sorption data

The amount of sorbed pollutant on the solid phase (q_e) can be plotted as a function of remaining concentration of

pollutant (C_e) in the aqueous solution at the equilibrium state and this relationship can be represented mathematically by many sorption models such as Langmuir (Eq. (3)) and Freundlich (Eq. (4)) models. The sorption data were fitted with these models using the Solver option in Microsoft Excel 2016 to find the constants of each model. The forms of these models can be written as follows:

$$q_e = \frac{q_{\max} b C_e}{1 + b C_e} \quad (3)$$

where q_{\max} is the maximum sorption capacity (mg/g) and b is the contaminant affinity to the reactive material [30].

$$q_e = a_F C_e^{b_F} \quad (4)$$

where b_F is the intensity of sorption and a_F is a constant related to the maximum sorption capacity [31].

3.2. Models of breakthrough curves

Advection and hydrodynamic dispersion are the main mechanisms governed the migration of dissolved contaminant in the subsurface environment. These mechanisms can be represented by the partial differential “advection-dispersion” equation which can be solved theoretically and numerically depended on the complexity of the physical domain. There are several popular mathematical models utilized for solving the “advection-dispersion” equation and represented the relationship between the normalized concentration (C/C_0) and the time at a certain location along the tested column packed with the single bed [32]. Nonlinear forms of Thomas, Belter and Yan models are fitted with experimental measurements using the Solver option in Microsoft Excel 2016 to find the constants of each model. Thomas model (Eq. (5)) assumed that the Langmuir model is described as the sorption process and the dispersion in the axial direction can be neglected:

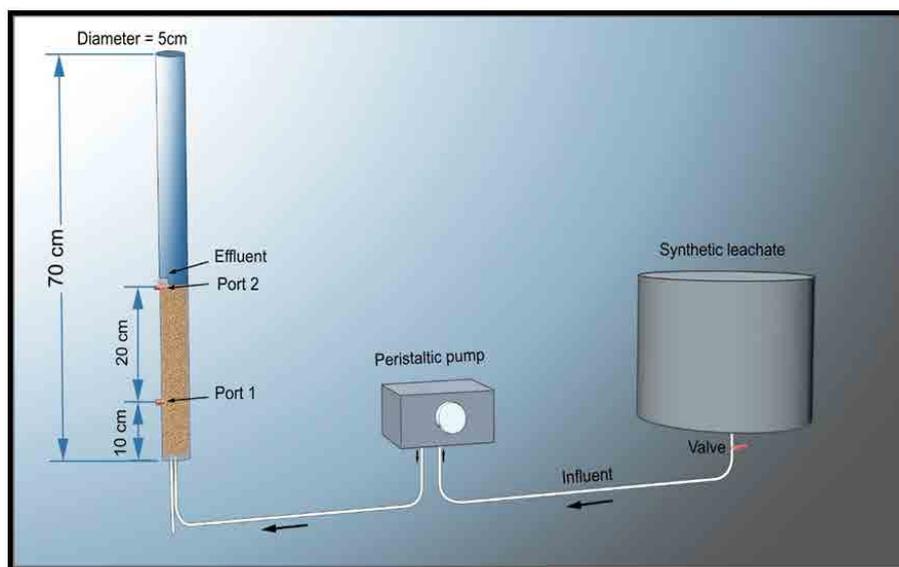


Fig. 1. Schematic diagram of the laboratory-scale column ($Q = 3$ mL/min, run time = 24 h).

$$\frac{C}{C_0} = \frac{1}{1 + \exp\left[\frac{(Mq_0K_{Th})}{Q} - \frac{K_{Th}C_0t}{1,000}\right]} \quad (5)$$

where M is the mass of sorbent packed in the column (g), Q is the flow rate of the aqueous solution injected to the column (mL/min), C_0 is the influent concentration of pollutant (mg/L), q_0 is the maximum sorption capacity (mg/g) and K_{Th} is the rate constant of Thomas model (mL/min mg).

The form of the Belter model is [33]:

$$\frac{C}{C_0} = \frac{1}{2} \left(1 + \operatorname{erf} \left[\frac{(t - t_{0.5})}{\sqrt{2}\sigma t_{0.5}} \right] \right) \quad (6)$$

where $t_{0.5}$ is the time required for C/C_0 to be 0.5, t is the column residence time, and σ is the slope of the breakthrough curve.

Finally, Yan model is also called in the previous studies as Dose-Response model and its formula can be explained below [34]:

$$\frac{C}{C_0} = 1 - \frac{1}{1 + \left(\left(\frac{Q \times C_0}{q_0 M} \right) \times t \right)^a} \quad (7)$$

where Q is the flow rate of the influent contaminated water (L/min) and a is the slope of the curve related between C/C_0 and t .

4. Results and discussion

4.1. X-ray diffraction analysis

The waterworks sludge was characterized using the XRD conducted in Germany Laboratory, Geology Department, College of Science, University of Baghdad, Iraq. Fig. 2 shows that the silica, calcite, and feldspar are the main components for this sludge with proportions of 78.2%, 17.3%, and 4.5%, respectively. The silicon dioxide (SiO_2) is the major constituent of silica and the sand in the waterworks sludge has resulted from the sedimentation process. The presence of quartz can be enhanced the removal of the cations through ligand complexation due to developing a negative charge on the sludge [35]. The presence of calcite, that is, CaCO_3 , in the sludge may have a role in the removal of $\text{NH}_3\text{-N}$, even with low value [36]. In spite of the aluminum is formed the principal constituent of the feldspar, but it is the percentage is very low and this may be due to adding low quantities of alum to raw water through coagulation–flocculation processes, however, this percentage of aluminum was able to remove of heavy metals. According to the previous studies, the concentration of aluminum in the leachate samples depends primarily on the pH of the aqueous solution and

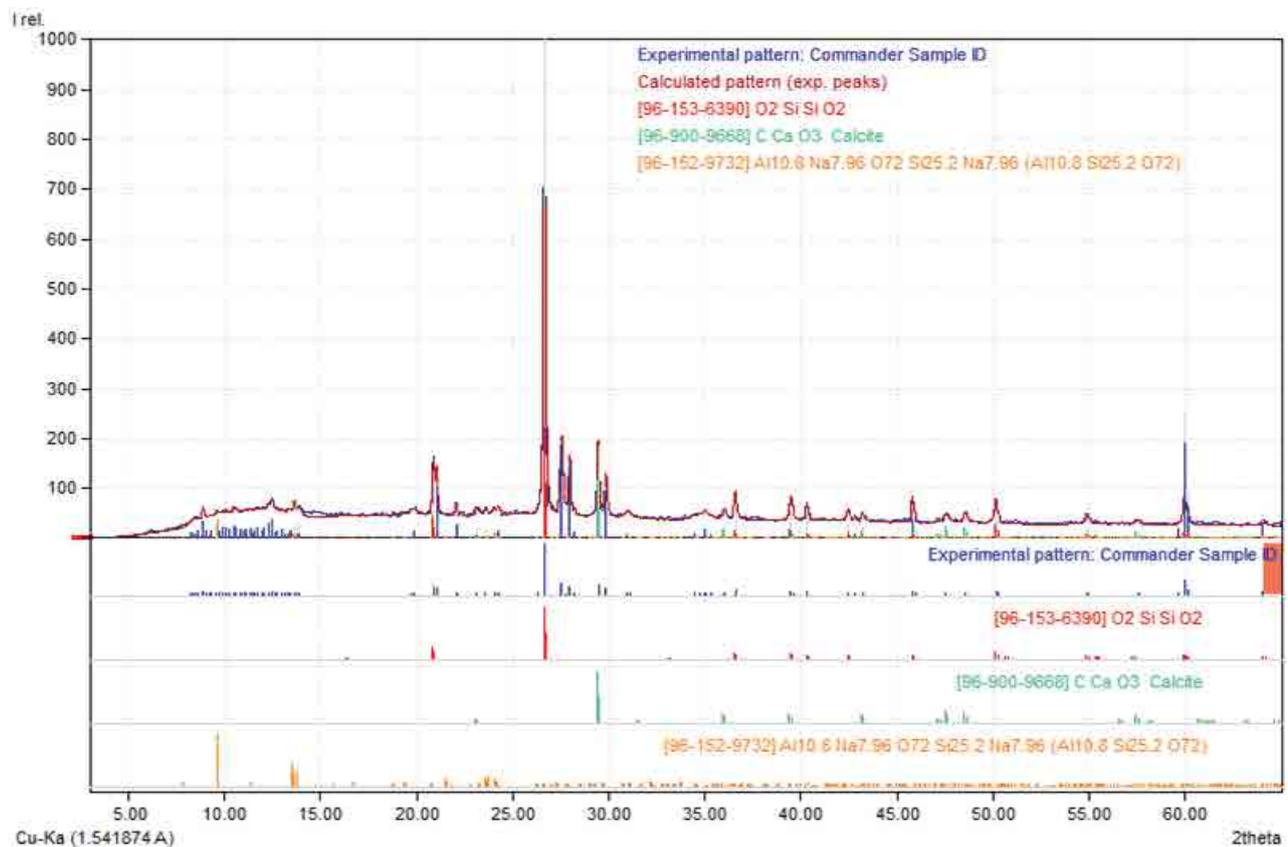


Fig. 2. X-ray diffraction (XRD) analysis for waterworks sludge used in the present study.

the aluminum leaching rate can be improved with increasing acid concentration. However, the concentration of aluminum released in the leaching process can be expected very low for adopted pH (≥ 5.5) because the aluminum with SiO_2 as well as other inert constituents will form an interdiffusion layer in the waterworks sludge and thus become the major limiting factor that controls the Al(III) leaching process as proved by Cheng et al. [37].

4.2. Waterworks sludge

Fig. 3a shows the variation of cadmium removal efficiencies as a function of sludge dosage. The removals are increased from 37.5% to 97.5% when the dosage changed from 0.5 to 20 g, respectively. This is logical behavior because of the higher dose of sorbent, the greater availability of vacant sites [38]. The results proved that 5 g of sludge was sufficient to achieve the removal efficiency equal to 93.6% and no more significant increase in this removal can be recognized due to an increase of sludge quantity, therefore, 5 g will be used as the best dosage in the next experiments.

Fig. 3b signifies that there is a rapid increase in the removal efficiency through the initial stages due to the presence of vacant sites and this removal becomes gradually constant after 30 min ($\approx 92\%$) until it reached 94% after 2 h.

Additional tests proved that little decline occurred in the removal efficiency of cadmium ions onto the waterworks sludge when the Cd(II) initial concentration had increased from 50 to 100 mg/L with a corresponding removal efficiency of almost 86%. The decline in the removal efficiencies will continue until to reach the value of 65% at a concentration of 250 mg/L. This behavior because the higher the concentration is the higher the driving force for the mass transfer from the bulk solution to the surface of the sorbent materials and this will make no more sorption sites available particularly during the first stages of the process. Finally, tests proved that there is an increase in the removal efficiency of cadmium from zero speed with an efficiency of 49% to 250 rpm with 95% removal. The reason for increasing the removal efficiency of the contaminant with increasing the numbers of rpm impaired to the mass-liquid medium can be explained as the higher the speed of agitation; the higher the migration of metal ions toward the active sites on the sorbents.

The interaction of waterworks sludge with $\text{NH}_3\text{-N}$, and COD is illustrated in Fig. 4a and it is clear that this sorbent has the low ability in the removal of $\text{NH}_3\text{-N}$ and the maximum removal efficiency was not exceeding 29% when sorbent dosage equal to 90 g/100 mL. This removal percentage may be resulted from the increase of pH for an aqueous solution due to the presence of CaCO_3 in the composition

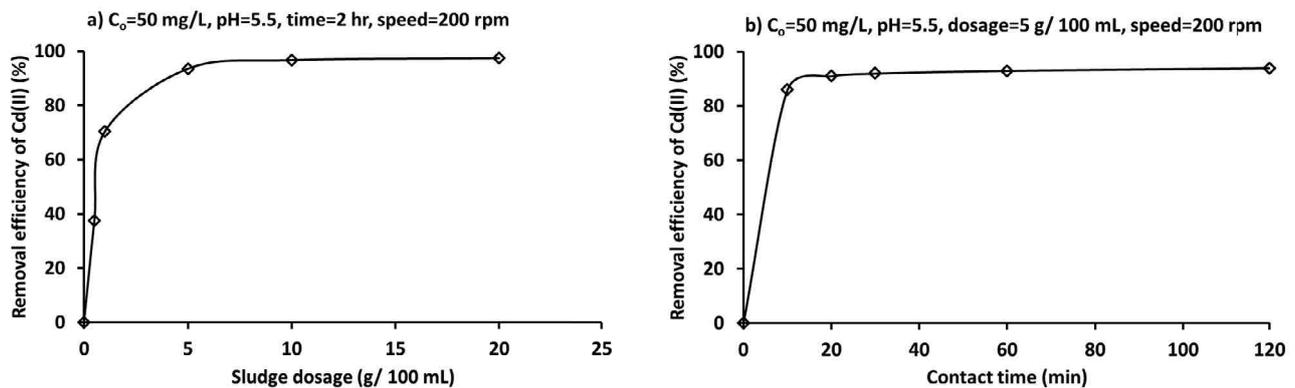


Fig. 3. Effect of dosage and contact time on the removal efficiency of Cd(II) for the interaction of waterworks sludge and contaminated aqueous solution.

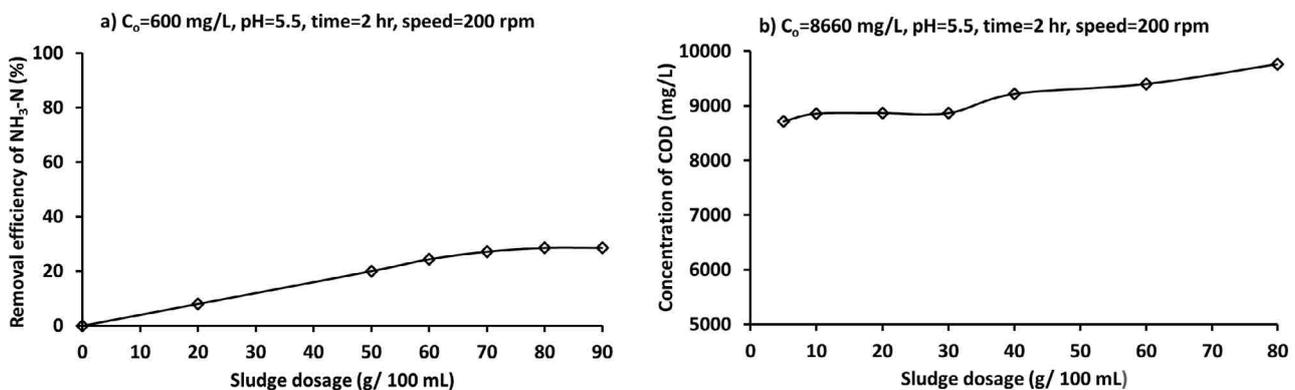


Fig. 4. Interaction of the waterworks sludge and aqueous solution contaminated either with (a) $\text{NH}_3\text{-N}$ and (b) dissolved organic matter (COD).

of used sludge and, accordingly, ammoniacal nitrogen is removed by air stripping [39]. However, the low efficiency may be due to the low affinity of $\text{NH}_3\text{-N}$ towards the sludge. Unfortunately, the results proved that the COD with an initial concentration of 8,660 mg/L was increased due to an increase in the sorbent dosage until arriving in the value of 9,760 mg/L at sludge dosage of 80 g (Fig. 4b). This can be attributed to the presence of organic matter in the composition of sludge and this results in agreement with many previous studies such as [40]. Indeed, when alum is added to raw water it flocculates as hydroxyl-Al species and organic matter as well as other insoluble impurities can be absorbed by aluminum hydroxide precipitates [19,41]. However, simple tests for the interaction of waterworks sludge and distilled water were conducted under the same operational conditions of the batch program. The results proved that there is an increase in the COD released from the sludge to the distilled water as a function of the sorbent dosage and this is consistent with findings of [42] for the same sorbent.

4.3. Commercial activated carbon

Fig. 5 illustrates that the removal efficiency of COD was increased from 13% to 69.5% due to an increase of CAC dosages from 5 to 70 g for an initial concentration of 500 mg/L. This increase may be due to the hydrophobic surfaces themselves; microspore structure, active surfaces and high sorption capacity that make CAC more efficient in the removal of organic contaminants [43]; however, the increase of dosage will be accompanied with stabilization of the removal efficiency. Also, the increase of initial concentration from 500 to 3,000 mg/L will increase of contaminant uptake from 0.676 to 2.615 mg/g. Results proved that this uptake is increased with increasing contaminant concentration, but conversely, this will decrease the removal efficiency of COD.

The removal efficiency of $\text{NH}_3\text{-N}$ is found to be not greater than 27% when sorbent dosage equal to 50 g (Fig. 5) and this value considers very low in comparison with the removal efficiency of COD using the same dosage of the sorbent. These results demonstrate that activated carbon does not have enough adsorption capacity for ammonia because

it usually possesses a non-polar surface due to manufacturing conditions at high temperatures, which is a disadvantage for some applications because of poor interaction with some polar contaminants. It is well known that ammonium ions are removed by the physical adsorption mechanism due to the wide range of pore sizes that are available on its surface [43–45]. Also, the sorption capacity in milligram of $\text{NH}_3\text{-N}$ per gram of CAC was decreased from 0.514 to 0.243 with increasing of sorbent dosage from 5 to 70 g/100 mL until reach the stabilization because there is an inverse relationship between them. Accordingly, the CAC can be adopted for treating the water contaminated with COD. So, the next task is finding the sorbent that has acceptable ability to remediate the water contaminated with $\text{NH}_3\text{-N}$ and this can be investigated through the section concerned the ion-exchange resin.

4.4. Amberlite ion-exchange resin

The relationship between the removal efficiency of $\text{NH}_3\text{-N}$ due to change of sorbent dosage from 0.5 to 20 g is plotted in Fig. 6 where the corresponding efficiency varied from 8% to 86%, respectively for initial concentration of $\text{NH}_3\text{-N}$ equal to 600 mg/L. The results can be explained on the basis that the resins are insoluble and contained exchangeable mobile ions. These ions are separated and became mobile when the resins come in contact with the contaminated water where the ions can be replaced via dissolved ions of contaminants to maintain on the neutral case. For example, the removal process is achieved due to the exchangeable between $\text{NH}_3\text{-N}$ and cationic resin mobile ion (H) [46]. Also, this figure shows the relationship between the removal efficiency of ammonia and contact time using amberlite resin. It seems that the removal percentage is increased with contact time in the first 5 min and, then, equilibrium can be achieved. After that, no significant change in the removal value can be recognized and this is consistent with previous studies [13].

4.5. Sorption isotherms

The relationships between the sorbed quantity of each pollutant (q_e , mg/g) and the equilibrium concentration (C_e)

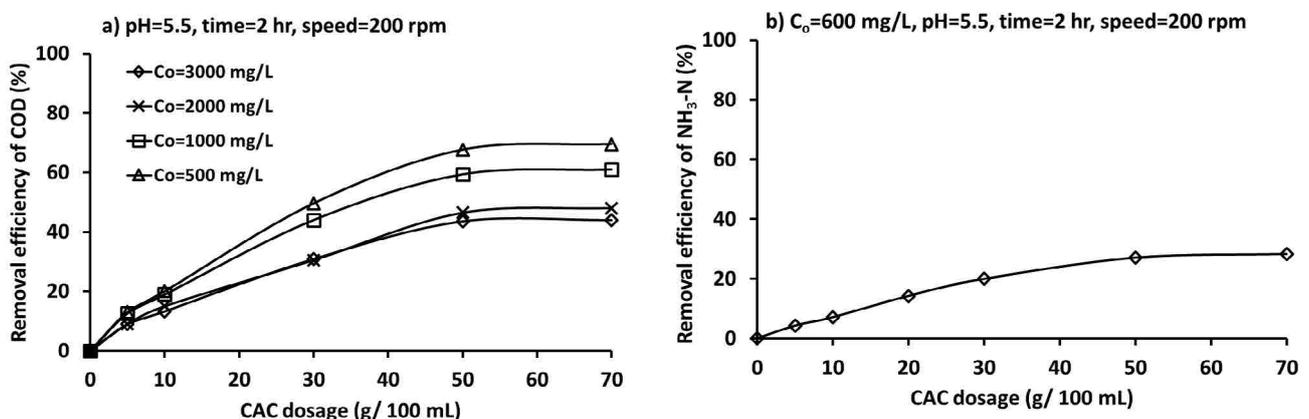


Fig. 5. Variation of COD and $\text{NH}_3\text{-N}$ removal efficiencies as a function of CAC dosage.

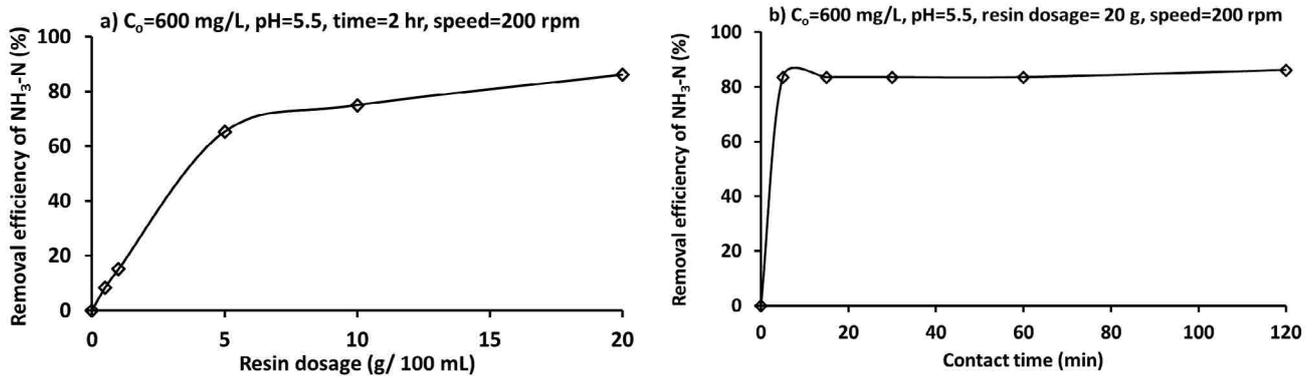


Fig. 6. Effect of resin dosage and contact time on NH₃-N removal by amberlite ion-exchange resin.

for representing the interactions of Cd(II) with sludge, NH₃-N with resin and COD with CAC are modeled using Freundlich and Langmuir models (Fig. 7). These models were fitted with measured sorption data and the constants of all models, as well as goodness parameters, are listed in Table 2. The statistical measures (i.e., sum of squared errors (SSE) and coefficient of determination (R)) signified that the Langmuir model can be used effectively to describe the quantities of Cd(II) and NH₃-N sorbed onto sludge and resin, respectively; however, the two models are able to

describe the sorption of COD onto CAC. The calculated maximum sorption capacities of the Cd(II) onto sludge, NH₃-N onto resin and COD onto CAC are equal to 5.634, 14.908, and 3.938 mg/g, respectively. The applicability of the Langmuir model means that the surfaces of sorbents are homogeneous where all the sorption sites assumed to have an equal sorbate affinity and the sorption at one site does not affect on the sorption at an adjacent site [47]. Also, it is clear that the values of Freundlich (or affinity) constants are greater than 1 and this certifies the occurrence of the favorable sorption [20].

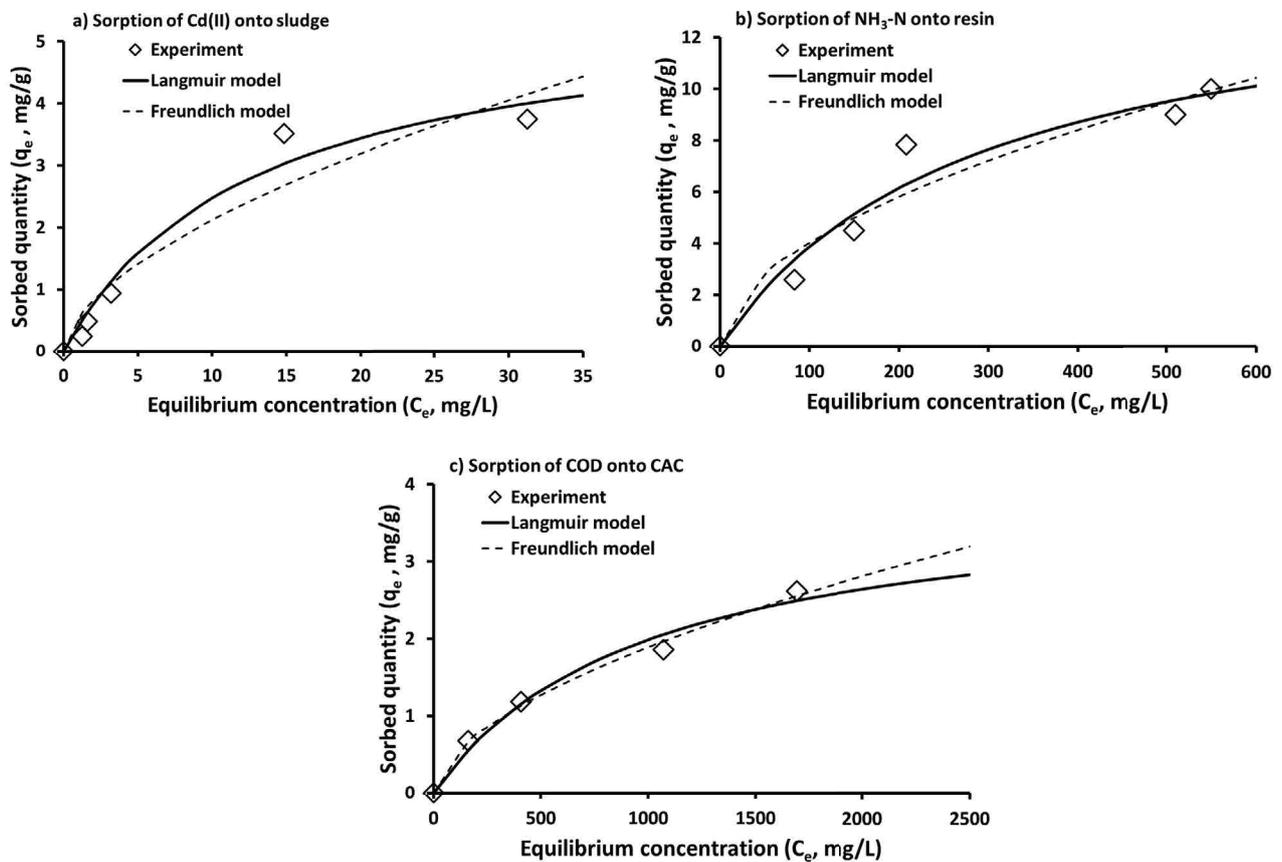


Fig. 7. Isotherms models for the sorption of (a) Cd(II) onto sludge, (b) NH₃-N onto the resin, and (c) COD onto CAC.

Table 2

Constants of isotherm models calculated in the present study for sorption of Cd(II) onto sludge, NH₃-N onto resin and COD onto CAC

Model	Parameters	Cd(II)/sludge	NH ₃ -N/resin	COD/CAC
Langmuir	q_{\max} (mg/g)	5.634	14.908	3.938
	b (L/mg)	0.0786	0.0035	0.0010
	SSE	0.4307	3.7425	0.0692
	R^2	0.9735	0.9524	0.9840
	a_F (mg/mg)(L/mg) ^{bF}	0.5490	0.3477	0.0366
Freundlich	b_F	0.5880	0.5316	0.5711
	SSE	1.0952	5.2705	0.0189
	R^2	0.9264	0.9323	0.9954

4.6. Continuous studies

The purpose of the column tests is to determine the efficacy of using beds with a height of 30 cm consisted of waterworks sludge, ion-exchange resin and CAC sorbents as PRB in the remediation of simulated leachate resulted from sanitary landfill. The evaluation process was achieved through the monitoring of normalized concentrations (C/C_0) for Cd(II), NH₃-N and/or COD with the travel time ($\leq 1,440$ min) in the P1 (10 cm) and P2 (30 cm) at flowrate equal to 3 mL/min (Fig. 8). The column tests were conducted using sludge (Fig. 8a), resin (Fig. 8b) and CAC (Fig. 8c) as PRB for synthetic leachate in the acetogenic phase. It is clear

from Fig. 8 that the increase of the bed height (i.e. adsorbent mass) means the pollutants had more time to contact with the sorbent and, consequently, a higher quantity of pollutant can be retained in the packed bed. Also, the increase of the adsorbent mass will increase the surface area and, definitely, the binding sites prepared for the sorption process [48]. Fig. 8a reveals that the waterworks sludge has the suitable ability in the containment of cadmium migration in comparison with ammonia-nitrogen front and the same trend can be recognized for these contaminants through resin bed as shown in Fig. 8b. Fig. 8c shows that the CAC has the significant ability in the restriction of the transport of Cd(II) and COD plume, however, the low efficiency was recognized for

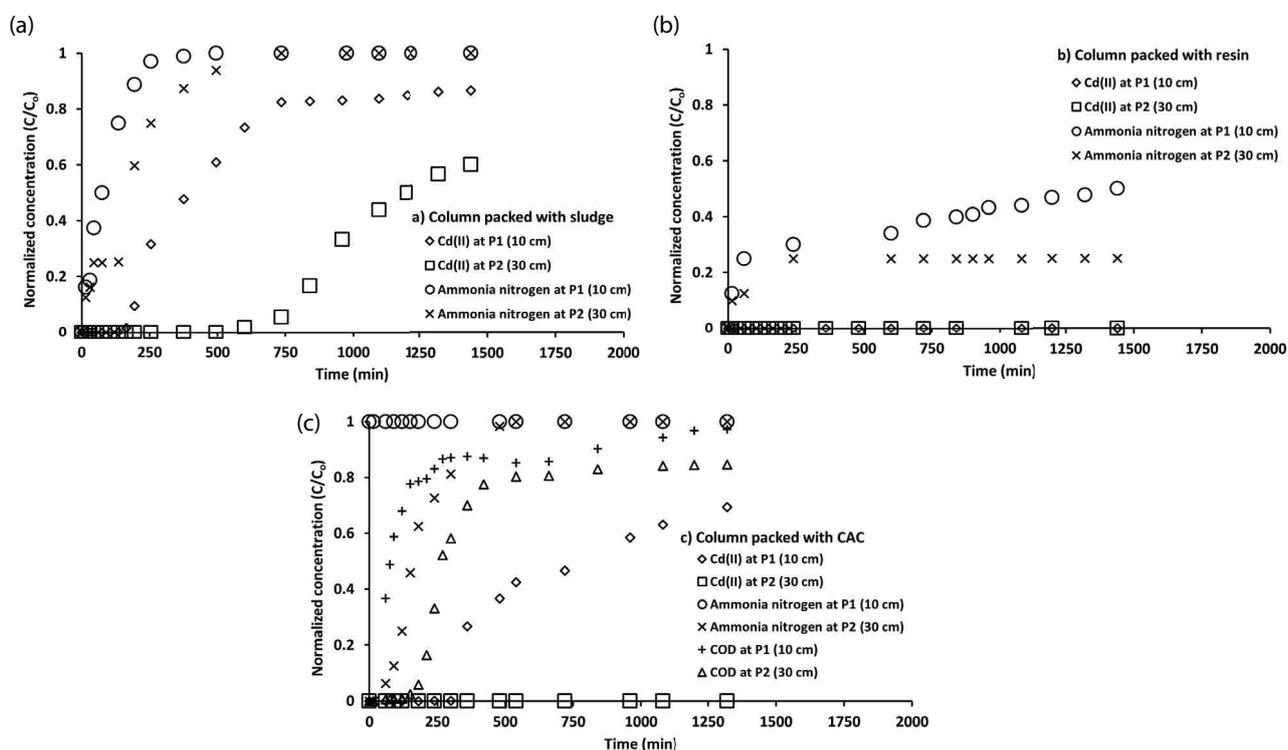


Fig. 8. Breakthrough curves for sorption of Cd(II), NH₃-N and COD onto (a) sludge, (b) resin, and (c) CAC packed columns at the ports P1 and P2.

containment the propagation of $\text{NH}_3\text{-N}$ plume. This may be due to the high affinity of Cd(II) and COD to the CAC in comparison with an affinity of $\text{NH}_3\text{-N}$. Fig. 8 elucidates that the appearance of breakthrough curves for Cd(II) through CAC and resin is required additional time and, consequently, the longevity of these sorbents to the heavy metal is longer than other studied cases. Also, the same phenomena can be recognized for the interaction of the $\text{NH}_3\text{-N}$ with ion-exchange resin and this means that the experiment must be extended for additional time to complete the S-curve.

Longevity can be defined as the required time for maintaining the concentration of contaminant downgradient of the barrier as less than the quality limit prescribed for drinking water and this term is equivalent to the “breakthrough time” calculated from “breakthrough point” on the breakthrough curve. Any desired value for normalized concentration such as the environmental acceptable limit or 5% can be adopted for identifying the breakthrough points. Using 5% as acceptable limit, the breakthrough time for the migration of COD in the CAC bed with depth of 30 cm is equal to 180 min, however, this value was decreased to become 50 min for $\text{NH}_3\text{-N}$ and, conversely, no definite value can be specified for Cd(II) through the same sorbent. The obtained results are consistent with batch results discussed in the previous sections where sludge, resin, and CAC are suitable for removing Cd(II) , $\text{NH}_3\text{-N}$, and COD , respectively.

Two additional multi-layered configuration bed tests (i.e. bed 1 and bed 2) were tested. The principal aim of these tests is finding the suitable and efficient configuration of a multi-layered bed that able to remediate simultaneously a wide range of contaminants included inorganic and organic compounds. Also, these tests are very important in finding the quantity of sludge, that is, inexpensive reactive material, that can be used as a substitute for traditional sorbents to maintain the required removal efficiency.

Fig. 9 signifies the normalized concentrations of the Cd(II) , $\text{NH}_3\text{-N}$, and COD resulted from the migration of the simulated leachate at the end of the bed 1 and bed 2. The decrease of the resin depth from 8 cm for bed 1 to 5 cm for bed 2 will decrease the time required to reach the same effluent normalized concentration of the $\text{NH}_3\text{-N}$, however,

the used depth of the sludge in the two tests has a good role in restriction the migration of Cd(II) metal. Also, this figure certifies that the increased depth of sludge from 2 cm for bed 1 to 5 cm for bed 2 will increase the effluent normalized concentration of the COD and this may be due to release a certain quantity of organic matter from this sludge as described previously in the batch tests. Accordingly, bed 1 can be adopted as a suitable choice to remediate the leachate contaminated with major three contaminants that simulated the organic and inorganic compounds.

Finally, monitoring of accumulated volumes of effluent treated aqueous solution for all used beds as a function of time was achieved and results proved that the relationship between the volume and time can be represented by ascending linear regression. This means that the hydraulic conductivity (calculated by Darcy’s law) of all beds are remained approximately constant for achieving the acceptable permeable condition without the loss of the reactivity because these beds can create connected pores not subject to infilling by biological growth and biochemically driven mineral precipitation products [49].

4.7. Modeling of breakthrough curves

The breakthrough curves are considered the key for characterization of the temporal remediation along the bed and this is very fruitful in the design of the barrier. Finding the best model for representing the measured observations is very important in specifying the breakthrough points which can’t be determined from these observations because of the presence of scattering. This can be achieved through the calculating of the agreement between theoretical predictions and measured values based on the SSE and R . Table 3 presents the parameters of the adopted models corresponding to the experimental conditions and goodness coefficients. In comparison with Thomas and Belter’s models, it seems that the Yan expression is more representative because it has the best values of SSE and R . Also, the breakthrough curves elucidated that the increase of bed depth (i.e., the quantity of reactive material) will increase the longevity of the bed for restriction of the simultaneous migration of Cd(II) , $\text{NH}_3\text{-N}$, and COD . However, the experimental

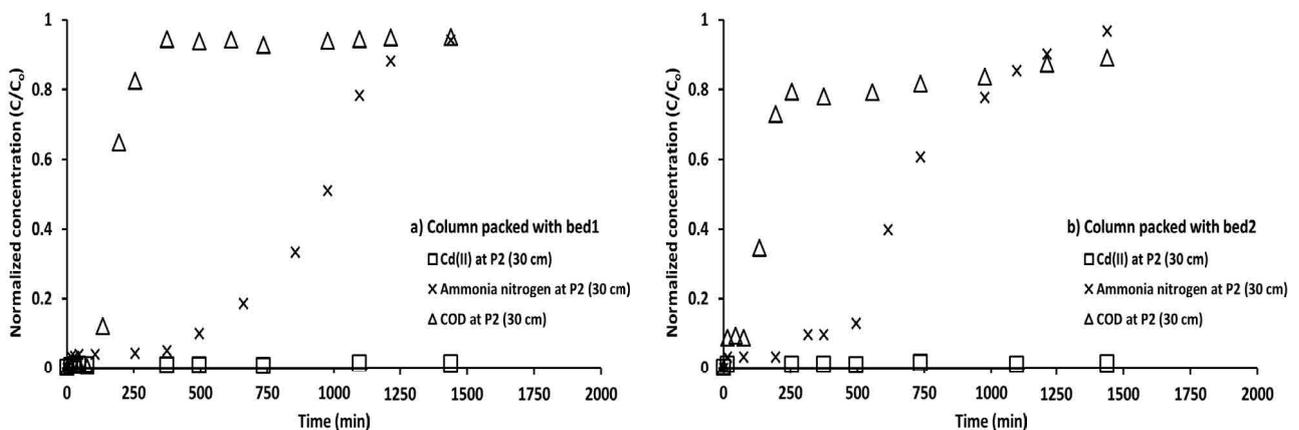


Fig. 9. Normalized concentrations of Cd(II) , $\text{NH}_3\text{-N}$, and COD onto (a) bed 1 and (b) bed 2 at the port P2.

Table 3
 Constants of breakthrough curves for sorption of adopted contaminants onto selected sorbents at P1 and P2

Models	Parameters	P1									P2								
		Cd(II)/sludge			NH ₃ -N/resin			COD/CAC			Cd(II)/sludge			NH ₃ -N/resin			COD/CAC		
		200*	30*	3'	165*	544*	3'	129.5*	8700*	3'	600*	30*	3'	495*	544*	3'	442*	8700*	3'
Thomas	$M_{q_0}k_{Th}/Q$	3.20253			1.49459			1.78812			4.85736			1.49556			4.55782		
	$K_{Th}C_0/1,000$	0.00698			0.00116			0.01892			0.00393			0.000395			0.01542		
	SSE	0.18403			0.053103			0.177518			0.034885			0.050524			0.21901		
	R ²	0.96578			0.79932			0.93060			0.96528			0.53282			0.97023		
Belter	$t_{0.5}$	395.9			1440			78			1200			2880			266.8		
	σ	0.49752			1.14094			0.98418			0.34090			1.03387			0.33215		
	SSE	0.21919			0.05901			0.22379			0.03285			0.04813			0.26986		
	R ²	0.98668			0.80859			0.95648			0.97338			0.52802			0.99075		
Yan	$Q \times C_0/q_0 \cdot M$	0.00238			0.00049			0.01286			0.00082			5.83774E-07			0.00333		
	a	2.24103			0.44682			1.41757			3.97962			0.14147			3.10338		
	SSE	0.04927			0.01175			0.02288			0.01540			0.009802			0.14577		
	R ²	0.98535			0.97077			0.98740			0.98359			0.90577			0.96417		

Superscripts (*, +, and ') are represented the M (g), C_0 (mg/L) and Q (mL/min), respectively.

data for multi-layered beds (i.e. bed 1 and bed 2) can't be formulated using mentioned models because these models are derived for bed consisted of one material.

5. Conclusions

- Batch study proved that the waterworks sludge can be used as an effective sorbent for remediation of aqueous solutions contaminated with Cd(II). The best-operating conditions that achieved 93% removal efficiency of Cd(II) for initial concentration 50 mg/L with pH = 5.5 ± 0.1 (simulated acetogenic phase of leachate) were; dosage 5 g/100 mL, agitation time of 30 min and shaking speed of 200 rpm. However, this sorbent was not suitable for removing NH₃-N, and COD. The CAC can be removed 69.5% of the COD, while, the ion-exchange resin was more suitable for remediation of aqueous solution contaminated with NH₃-N with the efficiency of 86%.
- The sorption process for all adopted contaminants is described by the Langmuir model with maximum sorption capacities of 5.634, 14.908 and 3.938 mg/g for Cd(II) onto sludge, NH₃-N onto resin and COD onto CAC, respectively.
- The results of the columns packed with a single bed are compatible with the results of the batch tests described in point (1) for synthetic leachate. These results proved that types of contaminants and sorbents play a significant role in specifying the longevity of the barrier. Also, the multi-layered column scheme can be considered a good application for the remediation of simulated leachate.
- In comparison with Thomas and Belter models, the Yan model was more representative for finding the propagation of adopted contaminants in the single bed packed column, however, the multi-layered beds cannot be formulated using breakthrough models because they are derived for bed consisted of one material.

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